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SUBCRITICAL AND SUPERCRITICAL FLUID EXTRACTION: A CRITICAL REVIEW OF ITS ANALYTICAL USEFULNESS

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ABSTRACT

Subcritical R134a is suggested as a low-pressure alternative to supercritical CO_2 in the supercritical fluid extraction technology in particular of palm oil application. Therefore, a measurement of solubility of palm oil in subcritical R134a will be carried out at temperatures of 40, 60, 70 and 80 °C and pressures up to 300 bar. The solubility of carotene are also will be measured using UV Spectrophotometer. Results obtained from this study will be compared with the previous work and for the first time, simulation for the SFE process of palm oil will be performed using Artificial Neural Network (ANN) and it will be implemented in comparisons as well when the operating conditions of the previous findings are different from this study. It is expected that the solubility of the palm oil in subcritical R134a is much higher than SC-CO_2, and it is expected that R134a could be a viable alternative solvent to supercritical carbon dioxide as R134a could be perform well at a lower pressure used whereas can achieved a higher solubility compared to SC-CO_2

Key Words: Subcritical R134a, Supercritical Carbon Dioxide (SC-CO_2) extraction, solubility, palm oil, carotene, artificial neural network (ANN)

1.0 INTRODUCTION

A supercritical fluid extraction (SFE) is an extraction carried out using a supercritical fluid. High demand for good quality oils urged researchers to find safer techniques for the extraction of the desired components while at the same time reduced thermal degradation and solvent contamination to a minimum. Hence, supercritical fluid extraction (SFE) is rapidly developing and a fast technique that has great potential separating and purifying high value products such as tocopherols, carotenoids. By using SFE technology the recovery or extracting analytes is precisely and reliability compared to conventional method i.e. Soxhlet extraction as isolation of the analytes are complete. This is because of the solvent power, polarity and working temperature of SCF, as well as its high diffusivity which is similar to a gas and this contribute to the chief factor on which complete extraction relies. At the same time, crude oils obtained by supercritical fluid extraction easily be refined than conventionally extracted oils as they contain fewer impurities [1].

In fact, several studies on SFE also has been applied to recover valuable minor components i.e. carotene and tocopherol by numerous researchers as they realized the importance of the compounds. Therefore, to ensure SFE technology is reasonable to the processing, it is important to have information about experimental equilibrium data (i.e. equilibrium solubility, phase equilibrium), fluids dynamics and mass transfer. Within the past decades numerous industrial and academic research and development laboratories have investigated the underlying fundamentals and process application of supercritical

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fluids extraction using a conventional solvent such as CO_2, propane in sub and/or supercritical condition [2]. However, there are only few of review papers studied the fundamental and process application using refrigerant as a supercritical extraction solvent [3-8].

1.1 Problem Statement

In the current research, numerous of SFE applications investigation has been performed and focused on using CO_2 as a supercritical solvent to investigate the capability of the solvent in fluids separation technique in palm oil application [11-13] and as alternative separation to conventional method i.e. Soxhlet extraction. In fact, supercritical CO_2 has been accepted as a common and standard supercritical solvent to many researchers. However, there is a major drawback on the use of CO_2 as a solvent for industrial scale due to the requirement of extreme high pressure operation in the region of between 200 to 300 bar and sometimes up to 500 bar. The high pressure operation can contribute to the high capital cost and also operating cost to maintain the high pressure. This is one of the factors that have contributed to the limited acceptance of SFE process using CO_2 to be commercialized in industrial. Thus, it is envisioned to discover for other solvent that might operate at the lower operating pressure than supercritical carbon dioxide needed. Therefore, in this study, subcritical R134a is suggested as a low-pressure alternative to supercritical CO_2 in particular of palm oil application since from the previous research [3-8] reported that it could perform as a good solvent and at the same able to extract analytes of interest at low temperature.

1.2 Objective

a. To investigate the applicability of an alternative sub-critical solvent R134a to SC-CO_2, extraction in palm oil application
b. To investigate the Artificial Neural Network simulation method for supercritical fluid extraction process.

1.3 Scope of Work

a. Determination of palm oil solubility in sub-critical R134a by supercritical fluid extraction experimental.
b. Identification of valuable minor components extracted i.e. vitamin A (carotene) using UV-Spectrophotometer.
c. Solubility of palm oil and carotene performance analysis as a function of temperature, pressure.
d. Development of Artificial Neural Network (ANN) system to simulate supercritical fluid extraction processes on the basis of Matlab software – to perform comparisons with previous study on the solubility of palm oil in supercritical carbon dioxide when the operating conditions are different from this work.

1.4 Hypotheses

a. Subcritical condition of R134a is able to perform in measurement of solubility of palm oil.
b. Temperature above T_c should be considered if the solubility in sub-condition is seems relatively low but careful in the usage is important as valuable minor components will deteriorate at high temperature.

c. Subcritical R134a is a viable as an alternative solvent for supercritical carbon dioxide when R134a could perform very well at a lower pressure and can attain much higher of solubility than SC-CO_2.
d. If solubility of palm oil in subcritical R134a is lower than SC-CO_2, however, in economically speaking, usage of R134a is one of advantage as it could reduce the operating cost and capital cost as it is require less pressure compared to SC-CO_2.
e. Solubility is higher either at higher pressure and constant lower temperature (because of density factor) or at higher temperature and some range of pressure, probably at higher pressure (because of vapor pressure factor).
f. Solubility of carotene in R134a slightly higher than SC-CO_2 since a polarizability parameter factor of solvent (R134a) should be considered as it will enhance the extractability of solutes into solvent as a greater polarizability will increase its solubility [14].If free fatty acid in the raffinate phase is relatively low as standard prerequisite demand (0.1%), thus R134a have a potential to be applied in the deacidification process of palm oil.
g. An Artificial Neural Network (ANN) could execute a simulation of operating conditions different from this study as it can perform a generalization when it is producing reasonable outputs for inputs not encountered during training (trained with experimental data) process.

1.5 Expected Contribution

The potential contributions that are expected to emerge from this work include:

a. Urged further researches in exploring and investigation a fundamental study such as phase equilibrium of palm oil- R134a system in a wide temperature and pressure range and next could led them to study a thermodynamic model of the system.
b. Major contributions in the area of palm oil quality production with a by integrating milling and refining process and recovery a valuable minor component using R134a as alternative solvent in palm oil refining could improve the profitability with a simpler, cost effective, and environmental friendly and efficient.
c. A new application of neural network into supercritical fluid extraction process in particular of palm oil usage.

2.0 SUBCRITICAL AND SUPERCRITICAL FLUID EXTRACTION

2.1 Supercritical Carbon Dioxide Extraction

Carbon dioxide is the commonly supercritical fluid (SCF) used as a solvent in food applications. It is not only cheap and readily available at high purity, but also safe to handle and very low levels in at which it is present in foods because it is easily removed by expansion to common environmental pressure values. In despite, of the fact, those practical advantages of CO_2 are also same as R134a. Carbon dioxide becomes supercritical at 31.1 °C and 73.8 bar. In contrast, the critical temperature of R134a is higher than CO_2 i.e. 101.4 °C (and critical pressure 40.6 bar), however, the experimental conditions are sufficiently enough at near the critical temperature as the compressibility is substantial good in order to obtain a variation of solubility data [8]. And the use of new

near-critical solvents, with the same benefits of CO_2 but substantially lower operating pressures, could increase the applicability of near-critical fluids as solvent [3]

It is preferred to operate at or near the critical temperature of the supercritical fluid and to adjust the pressure in order to obtain optimal fluid density for the extraction to be carried out. However, it will sometimes be necessary or desirable to operate a separation or extraction at higher temperature in order to increase the diffusion rate of the supercritical fluid and/or the component to be extracted, or to increase the volatility of the components to be extracted [5]. In contrast, it is reported that, the solubility in the subcritical (liquid) fluid (solvent) increases at constant pressure up to temperatures slightly below the T_c of the solvent [15]. In fact, in many cases, the enhancement of the solubility is especially significant near critical temperature of the solvent [16]. Figure 1 show a location of subcritical region in an example of phase diagram of substance.

Non polar and scarcely polar solvents with moderate critical temperature (e.g. N_2O, CO_2, ethane, propane, pentane, xenon, SF_6, and some freon) have a limited dissolving power for solutes of a highly polarity or molecular weight [17]. Thus, small proportions of modifiers are added to enhance their dissolving power. However, the addition of polar entrainers such as methanol to enhance the solubility polar compounds into CO_2 which is highly non polar solvent that could increase the effective critical temperature, and hence would lead to requiring higher extraction temperature and this can damage thermally labile products. Also, solvent modifiers may also need a downstream separation to obtain a pure product. In contrast, R134a is a naturally polar solvent and thus the solubility of polar compounds into R134a is rather sufficient.

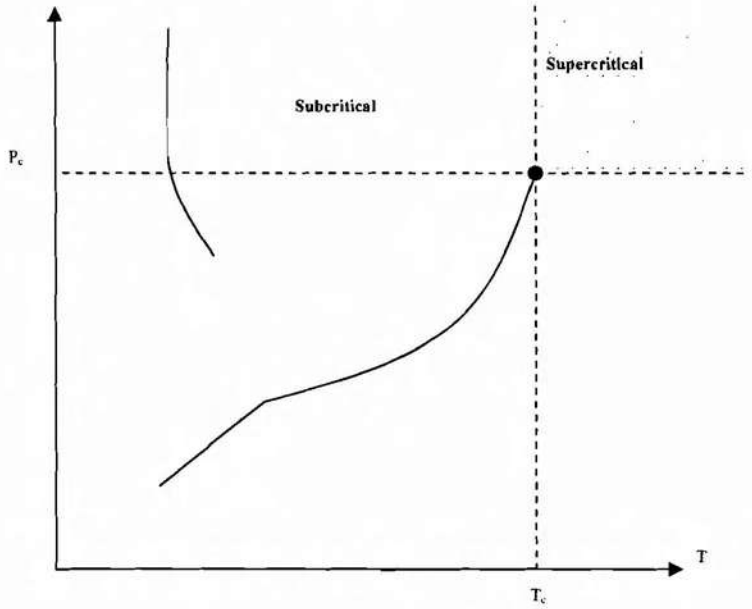

Figure 1 An example of phase diagram indicating a point of supercritical and subcritical region

Another factor in determining the choice of supercritical fluids is the thermal stability of the extracted compound at the working temperature. Therefore, a low a critical temperature is usually desirable, particularly with thermo labile analytes. Though, this

criterion apparently is not appropriate to R134a since its critical temperature is low enough i.e. 101.4 °C to avoid the thermal instability of coexisting phases and though near critical conditions is usually employ as the extraction is performed.

The polarity/polarizability parameter π^* value in the liquid region increases roughly linearly with increasing pressure in the liquid state and the value of π^* decreases dramatically at temperature above 100 °C and below 60 bar. Therefore, R134a shows a large change in solvent properties over a relatively small temperature and pressure range, suggesting that it would be a useful solvent for extraction purposes [17].

2.2. Subcritical R134a Extraction

Hydroflourocarbons (HFCs) are molecules containing only atoms of hydrogen, fluorin and carbon and were known to have effectively zero ozone depleting potential (ODP) at the time of the Montreal Protocol was established. In the automotive industry, R134a has been used in the air-conditioning system in vehicles, and at the same time it is also has been applied as aerosol propellants. In fact, R134a is approved for food use in Europe in regulator terms and a wide range of R134a extracts are approved in Japan. Besides, Ineos Fluor has obtained generally regarded as safe (GRAS) affirmation for its food-grade R134a in the United States[18].

R134a (1,1,1,2-tetrafluoroethane) is non-toxic, non-reactive, non-flammable, and non-ozone depleting. It also has a high volatility and a boiling point at atmospheric pressure of -25.9 °C which means that it leaves negligible solvent residues in the products. R-134a is a non-flammable halogenated fluid, stable to aqueous acids and bases and it can be regarded as an aprotic which is in general chemical terms. It is immiscible with water and sparingly soluble in water (1500 ppm at 20 °C). R-314a is a gas at room temperature and pressure with a normal boiling point 247 K.

In recent years, the solvency of properties of R134a have been under examination with the focus being on the properties of the supercritical fluid [17], vapor-liquid equilibrium of the binary mixture carbon dioxide-R134a [19] and supercritical mixture of CO_2 and R134a [20]. In these mixtures, R134a has been found to be an effective co-solvent or modifier, acting to increase the solubility of polar solutes and to increase the eluotropic strength of the solvent mixture over that of pure CO_2. It has been also found that R134a can be used to extract a range of materials of natural origin [21]. Products that may be extracted include natural flavours and fragrances and nutraceutical extracts. The extracts obtained using R134a are generally low in colour, low in inert lipid content and high in the desired impact or active species with good recovery of the active ingredients from the raw materials. Extraction could be conducted anywhere within the liquid temperature range of R134a but is normally conducted around or below room temperature (i.e. 25 °C) [18].

Some study has been formulated that the high pressure and low-compressibility region, the solvating power of the six refrigerants (HFC: R32, R125, R134a and R152a, HCFC: R22 and R123) are greater than carbon dioxide [22]. Wilde patented processes of extraction of fixed and mineral oils using liquefied R134a [6] and iodotrifluoromethane [21] at the pressure range 20-25 bar and temperature 40-60 °C with or without co-solvent. It has been found that R-134a can be used to extract a range of useful products from a wide range of materials of natural origins. The solubilities of squalene and oleic acid in subcritical R134a are sufficiently high to enable the process to take place at substantially lower pressures than required for supercritical CO_2 [4]. In addition, the solubilities of triglycerides in subcritical R134a were found to be very low; therefore, the fractionation

of palm oil (which consists mainly of FFAs and triglycerides) to give refined quality palm oil could be achieved at low pressure and high solvent-to-oil ratios.

Because of high volatility of R134a, product recovery from solvent can be conducted efficiently at relatively low temperature, minimising the loss of volatile top-note components from the extract whilst achieving minimal solvent residues in the isolated product. Although supercritical fluids offer the capability to control the solvent selectivity or strength through control of the fluid density, this requires control of both the process temperature and pressure in order to achieve reproducible processing. Being a saturated liquid governed by equilibrium, R134a needs only its temperature or pressure to be controlled in order to control the conditions of extraction or product isolation. This allows far simpler control of the process [18].

It is surprisingly that HFC 134a though a very poor solvent for fixed (eg. palm oil) and mineral oils (eg. petroleum) at low temperature is actually a very much better solvent at elevated temperature [21]. At 40 °C for example, cocoa butter (a fixed oil which are comprises natural mixtures of mono-, di-, tri-glycerides, fatty acids, sterols (and their esters) and natural waxes) dissolves in HFC 134a to a substantial extent, despite the fact that at a temperature only a few degrees lower i.e. at room temperature cocoa butter does not dissolve to any appreciable extent in HFC 134a. HFC 134a is a very poor solvent at ambient temperature, but at elevated temperature its dissolving properties are improved somewhat but they are still relatively poor. Some solutes such as fatty acids and triglycerides are only slightly soluble even in hot HFC 134a i.e. a temperature of about 40 to 60 °C.

In invention of a process for extracting polynuclear aromatic hydrocarbons from a thermostat elastomeric seal reported that 1,1,1,2-tetrafluoroethane (HFC 134a) in supercritical state are suitable for use in supercritical fluid extraction [5]. The solvent power of supercritical HFC 134a can be readily tailored to the particular extraction or separation by adjusting the temperature and pressure of the supercritical phase such that the component or components that are to be dissolved and removed from a composition are soluble and the other component or components of the composition remain undissolved.

In economic perspective, R134a solvents seems to be more promising as the extraction pressure used was much lower than that for CO_2 and thus the capital cost of a fractionation plant using R134a should be considerably lower than that of a plant using CO_2 although selectivity of lipid (squalene) is much lower than SC-CO_2 [4]. In the same work, they found that the separation of squalene from triglycerides/glyceryl ethers fraction using subcritical R134a was feasible and the fractionation temperature increased the oil loading in R134a as well as the squalene purity of the extract products.

Table below present the previous study on applications of R134a a solvent in supercritical extraction technology. However, published data and work is scarce and limited, especially in the investigation of applicability of R134a in food application.

Table 1 Literature survey of the previous study on the application of R134a solvent in the SFE and liquid extraction

Temperature (K)	Pressure (bar)	References	Research Field
374 – 423	100 – 400	[5]	SFE
313	100 – 400	[7]	SFE
333 – 353	60	[4]	SFE
313 and 343	60 – 300	[8]	SFE
303 – 353	40 – 200	[3]	SFE
313 – 343	25	[6]	Liquid Extraction

3.0 MEASUREMENT OF SOLUTE, OIL AND SOVENT

3.1 Extraction of Carotene

Several studies have been carried out the extraction of carotene and solubility of the compound measurement within somewhat range of temperatures and pressures in order to identify the potential of the compound to be extracted using supercritical fluid extraction technology and in different sources or materials such as palm oil [13], β -carotene type I, trans, crystalline synthetic [14, 23], freeze-dried carrot [24], and β-carotene type IV from carrots [8].

The fractionation of crude palm oil in the range of 40-60 °C at 110-200 bar was studied [13]. They observed that initial sample of palm oil extraction were light in colour compare to later fractions being more intense in colour due to the present of carotene. They also reported that the solubility of triglycerides and carotene were low in the supercritical CO_2. Thus, carotene can only be concentrated in the raffinate phase of extraction. The solubility of carotene in ethane was reported that, is much better compared to SC-CO_2 due to its greater molar polarizability than SC-CO_2. The solubility of β-carotene in SC-CO_2 increases with pressure at constant temperature [14], however, the solubilities was rather low generally even supercritical CO_2 (i.e. non polar molecules) is quite suitable to dissolve non polar compounds, and results of research also indicated that the equilibrium solubility of β-carotene in SC-CO_2 is low [23]. This might probably due to high of molecular weight of β-carotene which become as a resistance to solvating properties of the solvent. The data for solubility of carotene and tocopherol in carbon dioxide are always been studied. Researchers always compare their results between the previous one to get the mutual solubility of the substance in SC-CO_2. These data are listed in Table 2.

A research on solubility of carotene in SC-CO_2 and in sub-critical halocarbons in terms of temperature was conducted in a subcritical condition of R134a [20]. It was reported that, a little difference of β-carotene solubility was observed between halocarbons and SC-CO_2 as a solvent in supercritical extraction applications. There is much scatter in the literature data for β-carotene in CO_2, probably due to both to the very low solubilities and to problems with purity and stability [21]. Table 3 shows the solubility of carotene in R134a at various pressures and temperature of 40 and 70 °C. They described that the solubility is consider low because R134a is a polar solvent, while

the carotene is a non-polar compound. However, the difference solubility between two fluids are relatively little.

Table 2 Literature survey solubility measurements of carotene and tocopherol in supercritical CO_2

Systems-CO_2	Temp. (K)	Pressure (bar)	Ref.
Carotene	313, 333, 343	200-500	[25]
	298, 313	100-300	[23]
	310-340	100-260	[24]
	313, 323, 333	120-300	[14]
	313, 323, 333	300	[26]
	313, 323, 333	120-280	[27]
Tocopherol	298, 313	100-180	[28]
	298-333	90-260	[29]
	303-353	90-350	[30]
	313, 333	100-180	[31]
	313, 333, 353	80-290	[23]
	313, 333, 353	60-300	[32]

Table 3 Solubility of carotene in R134a [8].

Temperature, °C	Pressure, MPa	Concentration, Mol/dm^3
40	6.40	2.48×10^{-3}
	13.36	3.53×10^{-3}
	20.35	3.82×10^{-3}
	27.37	4.02×10^{-3}
	34.37	4.10×10^{-3}
70	6.83	1.02×10^{-2}
	13.67	1.23×10^{-2}
	20.59	1.38×10^{-2}
	27.44	1.44×10^{-2}
	34.29	1.46×10^{-2}

3.2 Measurement of crude palm oil solubility in supercritical solvent

A dynamic (flow through) technique approach will be applied in determining the solubilities of crude palm oil in subcritical R134a. The experimental set-up for the supercritical fluid extraction process is shown in Figure 2. It consists of a R134a gas cylinder in a liquid phase, a chiller (Yih Der, B/L-730) to cooling the R134a, a HPLC pump (Model PU-980, Jasco, Japan, a back-pressure regulator (Model 1580-88, Jasco, Japan) to control the system pressure, 50 mL extraction cell, a wet gas meter (WNK-1A,

Sinagawa Corp, Tokyo, Japan) to measure the flow rate of R134a used during extraction process and a analytical balance (Sartorius B31005, German). Commercial liquefied R134a gas was purchased locally from Malaysia Oxygen, Penang Malaysia (MOX) in a gas cylinder. Sample of crude palm oil was obtained from MALPOM Sdn Bhd, a milling palm oil at Seberang Perai, Penang. In the figure 2 below, *1* is represent as cylinder tank of R134a, *2* is chiller, *3* is pump (HPLC pump), *4* is a extraction cell is placed in the oven, *5* is extraction cell and *6* is wet gas meter for indicating of solvent flow rate used.

R134a from a cylinder tank will be cooled to liquefied gas R134a is fully in liquid phase and will be fed into a HPLC pump to compress the solvent until reach the desired pressure for the separation process. The compressed solvent is then fed into the extraction cell through input valve (the valve is not shown in the figure). The extraction process is start just after the solvent enter the cell and the system is maintained about 10 minutes before the exit valve is opened. The purpose is to allow the equilibrium condition exist between crude palm oil and solvent if possible. But, whether or not the equilibrium has been reached it will be checked by observation on graph of effect of solvent mass used on oil extracted.

During the extraction, the R134a flow rate will be varied and tested by trial and error to study their influence on the equilibrium conditions; the sluggish flow rate will present the equilibrium condition precisely, as a hypothesis and in order to maintain the desired pressure and temperature of the extractor. The volume of R134a passed through the extraction cell is recorded at atmospheric temperature and pressure at every collection time using a wet gas meter. Extraction will be carried out continuously for 60 minutes oil extracted which every 10 minutes run is considered as a fraction. Pressures of 60, 130, 200 and 300 bar, and temperature of 40, 60, 70, and 80°C are used in this study. There are 16 combinations of pressures and temperatures used, that is, temperature constant at 40°C varying at pressures of 60, 130, 200 and 300 bars

3.3 R134a Density Calculation

In this study, a density property is considered in order to obtain the mass of R134a solvent consumed during the extractability measurement. The solubilities of palm oil are then will be calculated from the gradient of the linear portion of the extraction curve since it is indicates the saturation solubility of palm oil-R134a system. Results from study [3] showed that the density of the saturation solvent phase was virtually the same as of the pure solvent. Thus, it is regard to be relevant to predict the R134a density using Peng-Robinson equation of state [3]. Therefore, the density of R134a solvent has been calculated using Peng-Robinson equation of state and the values are presented in table 5.

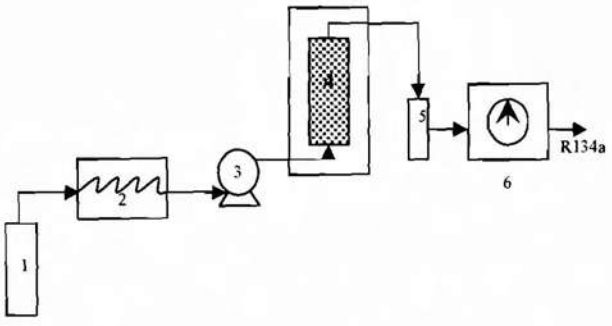

Figure 2 Schematic diagram of Supercritical Fluid

$$P = \frac{RT}{V - b} - \frac{a\,(T)}{V\,(V + b) + b(V - b)} \tag{1}$$

The Peng-Robinson cubic equation of state (1) is used to predict the density of R134a at the operating conditions in this work which also has been applied in [3] study. This cubic equation of state is commonly used since it has been generalized and offers reasonable predictive capabilities of liquid densities and has been used for a wide range of mixtures of nonpolar compounds and limited range of polar compounds. Equation (2) has been applied to obtain a reliable density data as a high polar compound, that is, a subcritical R134a which also has been used in [3] with temperature range of 303 to 353 K. In the original equation of PR-EOS, the pure-component a and b parameters are related to the critical properties and acentric factor, ω. The equation used to calculate the dependency of a upon ω was based on matching hydrocarbon vapor pressure to predictions from the equation of state [3]. The following equation has been used [3] to optimize the density and vapor pressure predictions of the equation.

$$a_i = a_c \left\{ 1 + f(\omega) \left(1 - \sqrt{\frac{T}{T_c}} \right) \right\}^2 \tag{2}$$

The density predictions for R134a using the standard b and a values calculated from equation (2) was compared with the tabulated data (i.e. An International Standard Formulation for the Thermodynamic Properties of 1,1,1,2-tetrafluoroethane for temperature from 170 to 455 K and pressures up to 70 MPa) in the subcritical and gaseous region to obtain an optimized value for $f(\omega)$ over the temperature range used [3]. The parameters used in the calculations are shown in table 4 and table 5 shows the density calculated at the range of temperature used in this work.

Table 4 Peng-Robinson Equation of State Parameters for R134a over the temperature range 303 – 383K

Parameter	R134a
MW, g mol^{-1}	102.30
T_c, K	374.21
P_c, bar	40.59
a_c, J m^3 mol^{-2}	1.1547
b, 10^3 m^3 $kmol^{-1}$	0.05923
$f(\omega)$	0.7202

Note: a_c, b and $f(\omega)$ obtained from [2]

Table 5 Density calculated using PR-EOS at varies of temperature and pressure

Temperature (°C)	Pressure (bar)	Density (kg/m^3)
40	60	112.74
	130	259.46
	200	426.16
	300	739.14
60	60	106.05
	130	241.16
	200	393.54
	300	660.67
70	60	102.55
	130	232.37
	200	377.25
	300	625.10
80	60	99.54
	130	224.85
	200	363.57
	300	596.53

4.0 Artificial Neural Network Simulation

An artificial Neural Network (ANN) is an information processing paradigm that is inspired by the way biological nervous system, composed of a large number of highly interconnected processing elements (neurons) whose function is determined by network structure, connection strengths, and the processing performed at computing elements or nodes. ANN could be developed to simulate SFE processes on the basis of Matlab software which has an ANN Toolbox, and though a special program can be build very conveniently as regards to the process systems of interest. On the basis of the experimental results, artificial neural network (ANN) technology was applied to the simulation of the supercritical fluid extraction of vegetable oil [32, 33]

Multilayer of feedfoward network is commonly used with back-propagation algorithm in architecture of the neural network. Figure 3 shows an example of feedfoward network, which β_h is weight between hidden and output layer and γ_{hi} is weight between input and hidden layer. Backpropagation is a kind of a steepest descent method of optimization [34]. The input layer will take in the data input vector, the output layer will be used for writing the output, and an intermediate (or hidden) layer that allows the increasing of the network memory, provides some flexibility. Owing to this architecture, the net is able to map linear and nonlinear relationships between input and output.

A major task for neural network is to learn a model of the world (environment) in which it is embedded and to maintain the model sufficiently consistent with the real world so as to achieve the specified goals of the application of interest. Basically, there are two kind of information in designing the neural network. A set of input-output pairs with each pairs consisting of an input signal and the corresponding desired output response, is referred to as a set of training data or samples. The training of the network is repeated for many examples in the set until the network reaches a steady state where there are no further significant changes in the synaptic weights, i.e. interneuron connection strength [35.36].

After the ANN system was trained by experimental data points, it then will be tested by another set of experimental data, which had not been seen before as samples. The results of the ANN calculations will be compared to those of the experimental data to demonstrate the applicability of this method.

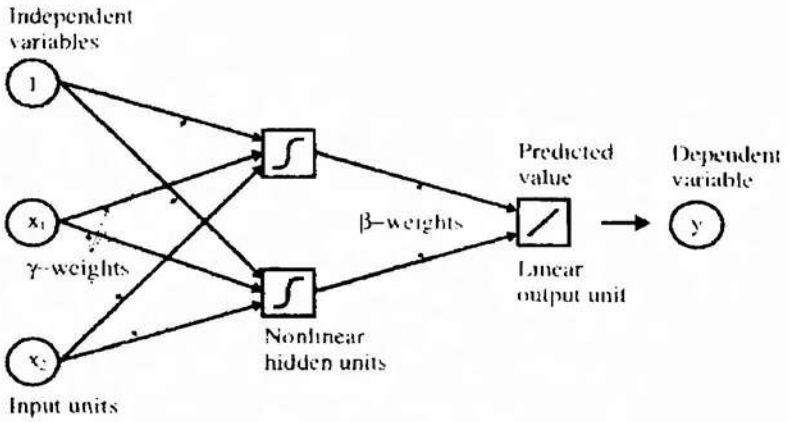

Figure 3 A Multilayer of Perceptron Neural Network

5.0 RESULTS AND OUTCOMES

In order to obtain a reliable solubility data, it is need to perform an experimental work as a prerequisite step including the investigation of the oil extraction yield. Though, in this work the oil extraction will be initially carried out during the experiment, and then the analysis of the oil extracted by solvent will be executed in order to identify the capability of the solvent to present a saturation condition with the components extracted. In fact, to consider a subcritical R134a as a viable solvent in supercritical fluid extraction technology, it is need to perform a comparison result obtained in this work with the previous study which has been using supercritical CO_2. This will be done by evaluating graphically and by Artificial Neural Network (ANN) when the operating conditions are different from this work.

5.1 Factor influenced oil yield extraction

There are three aspects will be considered in the discussions to investigate the performance of the oil yield as a function of time, temperature, pressure, and mass of solvent consumed.

5.2 Oil yield versus. time at Ti for different P

The discussion on this part is highly about the extraction rate behavior at the various combinations of temperature and pressure, and also to identify the highest rate of extraction among the operating conditions used. It is expected that at 300 bar and 80 °C indicates the fastest of the extraction rate. The rate of extraction is extremely rapid at the higher temperature and pressure [11].

5.3 Oil yield versus. R134a mass used at Ti for different P

This plot graph is required in order to obtain the solubility data at the operating conditions used i.e. at temperatures of 40, 60, 70 and 80 °C and pressures ranging from 60 to 300 bar. This graph also show the dependency of mass of oil extracted on the mass of the solvent consumed.

5.4 Oil yield versus. P for different T

Effect of the pressure on the oil extracted by subcritical R134a will be discussed at varies of temperatures used. It is expected that the extraction yield increase with the increasing pressure applied during the process. As reported, it was observed that the extraction yield strongly increased with pressure, according to the basic principles of supercritical fluid extraction [9].

5.5 Oil yield versus. T for different P

The influence of temperature on the oil yield extracted at the different pressure is also being investigated. The purpose is to observe the performance of the oil yield when temperatures are changes at varies of pressures, and also to identify the finest pressure which will present the highest oil yield among them. The reason is corresponding to the report [9] which the influence of temperature on oil yield or solubility is more significant than effect of density of solvent on oil yield or solubility.

5.6 Effect of Pressure and Temperature on the Solubility Performance

The pressure and temperature effects on the solubility performance will be discussed and clarified as those factors are known as fundamental facts in order to understand the solubility of many substances in supercritical fluids. This is because of the solvating power of the supercritical fluids is highly dependent on its temperature and pressure, and though, it is reasonable to discuss the solubility in manners in terms of temperature and pressure.
At the same time, a comparisons of solubility attained in this work will be perform using graphically and by simulation of ANN when the operating conditions are out of range than this work. The published data that are going to be compared including are, [8, 11, 12, 14, 23].

5.7 Pressure Effect on Solubility

It is expected that the palm oil solubility will increase as the pressure increase at a constant temperature. It is described that [1], near the critical pressure CO_2, the solubility increases sharply as result of the marked increase in density with pressure.

5.8 Temperature effect on Solubility

The solvent density and the vapor pressure of the oil depend on the pressure and temperature, and hence have an effect on the solvent power of solvent. When the temperature and pressure are varied, one of these two effects will become dominant and the next can be either decreased or increased. Some reported [3] on the investigation of lipid solubility using subcritical R134a showed that as the temperature increases to the

supercritical region, the density of the solvent will become less than that of the saturated lipid phase.

The solubility is expected to be increase markedly with temperature at high pressure. There were reported [11] that at 40 °C the solubility of the oil increases at relatively slower rate with increasing pressure whereas at higher pressure the solubility increased rapidly with increasing temperatures. In contrast, it is expected that the solubility will increase at of lower temperature and higher pressure (40 °C/300 bar) because of the solvent density is the highest among the other temperature and pressure. In [12] works, at the lowest temperature, that is, the highest solubility were reported when the pressure was being constant and the temperature was varied. However, vapor pressure of solutes factor must be take into account as when temperature increase, the solubility of the solutes also are increase. In fact, the highest solubility is achieved at the highest of temperature and pressure [11].

However, the effect of temperature on solubility is somewhat more complex since the phenomenon known as retrograde vaporization probably occurs. In the phenomenon, there is some range of the pressure where the solubility will decrease with increasing the temperature. This is because of the dependent of the solvent density on the temperature. When the temperature increase within that pressure range, the solubility is decrease as result to its density decrease as the temperature changes to increase. While at the other pressure range, the solubility is enhanced as the temperature rises due to the vapor pressure of the solutes increase. This phenomenon has been reported for the supercritical CO_2 situation [1], however, no reports on subcritical R134a applications in supercritical extraction technology are found about this phenomenon. Thus, observation and analysis of the results during the experiments will be performed to investigate the phenomenon whether occur.

5.9 Valuable minor component

Oil extracted from this study will be analyzed by UV/VIS Spectrophotometer for total carotene determination, that is, the concentration of carotene in the solvent at temperatures of 40, 60, 70 and 80 °C and pressures up to 300 bar. The absorbance will measured at a wavelength of 450 nm where carotene has the absorption maximum in n-hexane [14, 23].

5.10 Solubility of carotene

It is expected that the solubility of the carotene is increase with the increasing temperature and it is increase with the pressure in the temperature range used. The solubility of carotene increased with increasing temperature and pressure [11, 25]. In fact, above 60 °C when increasing pressure at constant temperature increases the solubility more markedly than increasing the temperature at constant pressure [11]. In contrast, it is reported that temperature had a little effect on the solubility of β-carotene in supercritical carbon dioxide [13]. However, results from this study will be observed as R134a is a naturally polar solvent, which it is expected that the solubility of β-carotene will be enhanced.

6.0 CONCLUSION

The outcome of expectations from this study are:

i. The solubility of palm oil in subcritical R134a is higher at constant lower temperature and higher pressure, i.e. (300 bar/40 °C). This is because the density at this condition is the highest and it is more dominant than vapor pressure of solutes. However, observation must be performed to investigate a complex factor of temperature effect on solubility since it is also could be higher at higher temperature and some range of pressure as vapor pressure is a dominant factor.
ii. Subcritical R134a is feasible in the extraction of carotene.
iii. Subcritical R134a is a viable solvent used in SFE technology.
iv. An Artificial Neural Network (ANN) – supercritical fluid extraction simulation systems (palm oil-R134a) will be successfully programmed and can predict the SFE process very well.

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